

Synthesis and Crystal Structure of a New *S*-Substituted Dicarba-*nido*-undecaborate Derivative (Inner Phosphonium Salt)

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The title compound, 7,8- μ -[SCH(PPh₃)S]-7,8-C₂B₉H₁₀, was prepared from the tetramethylammonium salt of 7,8-(1',3'-dithia-2'-ethoxypropane-1',3'-diyl)-7,8-dicarba-*nido*-undecaborate(12) and triphenylphosphine. The compound crystallizes in the monoclinic space group *P*2₁/*c* with unit cell dimensions *a* = 11.373(3), *b* = 14.654(3), *c* = 14.694(6) Å, β = 89.48(3)°, *V* = 2449(2) Å³, *Z* = 4. The structure was refined to a final *R* = 0.087 and *R*_w = 0.064 for 3021 reflections and 339 parameters. The positively charged phosphorus atom of the triphenylphosphonium unit, which is substituted in the five-membered sulfur heterocycle fused to the carbon atoms of the dicarba-*nido*-undecaborate cage, compensates the negative charge of the dicarborate.

Versatile ligands such as 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1 –) derivatives incorporating exocyclic *S,S'*-connected strings offer several coordination sites (the C₂B₃ open face, S groups and B–H units for the formation of exo-*nido* complexes). Generally, however, *S,S'*-coordination^{1–4} is preferred. In accordance with our hypothesis¹ that the length of the exocyclic string modulates the B(3)–M distance, novel B(3)–Rh σ -interactions⁵ and agostic B(3)–H→Ru bonds² with short –S(CH₂)_{*n*}–S– strings were obtained. In these complexes only one carborane ligand is coordinated to the metal, but bis-complexes with different symmetry are also known. In [N(CH₃)₄][Ru{7,8- μ -(SCH₂CH₂S)-7,8-C₂B₉H₁₀}₂Cl]⁶ the complex unit has C_s symmetry, whereas a Pd complex¹ with a longer string adopts C_i symmetry. To achieve a better understanding of the coordination behaviour of 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1 –) derivatives with short external *S,S'*-connected strings, we synthesized two new ligand derivatives of 7,8-(1',3'-dithiapropene-1',3'-diyl)-7,8-dicarba-*nido*-undecaborate(12). Respectively, these new ligands have an ethoxy unit and a triphenylphosphonium moiety attached to the CH₂ group, forming a C–O and C–P bond and yielding [N(CH₃)₄][7,8-(1',3'-dithia-2'-ethoxypropane-1',3'-diyl)-7,8-dicarba-*nido*-undecaborate(12)] (1) and 7,8-(1',3'-dithia-2'-triphenylphosphoniumpropane-1',3'-diyl)-7,8-dicarba-*nido*-undecaborate(12) (2). In the latter

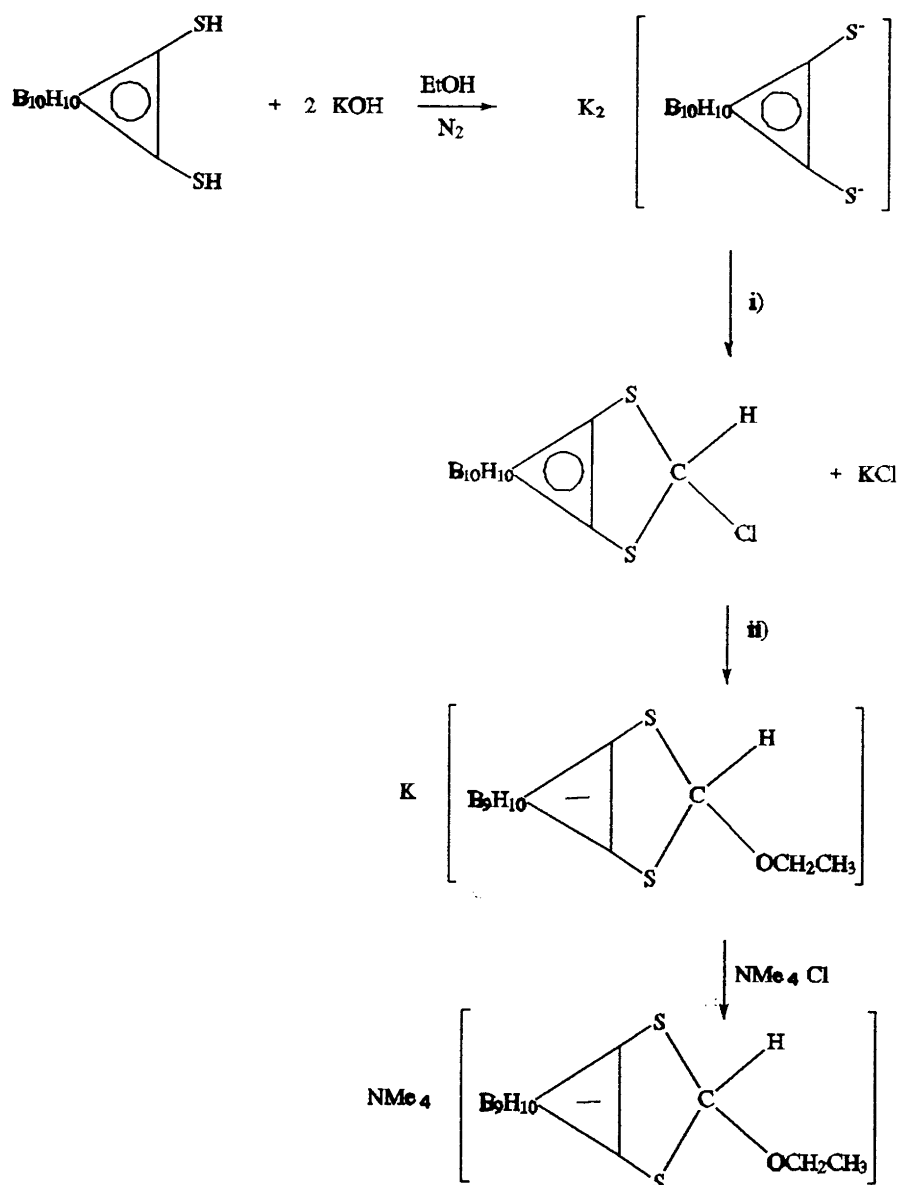
compound the positive charge on phosphorus compensates the negative charge on the carborane cage. Here we report the synthesis of both compounds and crystal structure of the latter.

Experimental

Synthesis. 1,2-Dicarba-*closo*-dodecaborane (Dexsil Chemical Corp.) was sublimed before use. From this, 1,2-dithiol-*o*-carborane and [N(CH₃)₄][7,8-(1',3'-dithiapropene-1',3'-diyl)-7,8-dicarba-*nido*-undecaborate] were prepared according to the literature.^{7,8} A 1.7 M solution of *n*-butyllithium in hexane (Fluka) was used as received. Ethanol was reagent grade. All other reagents (Fluka or Aldrich) were used as supplied. Elemental analysis was performed using a Perkin-Elmer 240-B microanalyser. The ¹H-NMR and ¹¹B-NMR spectra were obtained with a Bruker AM 400WB instrument, and IR spectra of KBr pellets with a Perkin-Elmer 240FT spectrophotometer.

Preparation and characterization of [N(CH₃)₄][7,8-(1',3'-dithia-2'-ethoxypropane-1',3'-diyl)-7,8-dicarba-*nido*-undecaborate(12)] (1) (Scheme 1). Under a dinitrogen atmosphere, 2.5 ml (31 mmol) of chloroform and 2.5 g of sodium iodide were added to an absolute ethanol solution of potassium 1,2-dithiolate-*o*-carborane prepared from 1,2-dithiol-*o*-carborane (500 mg, 2.40 mmol) and 350 mg

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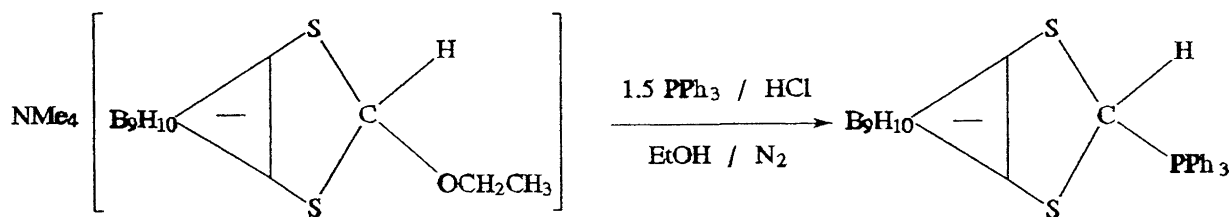


Scheme 1. Synthesis of **1**. (i) HCCl_3 , NaI, reflux (2 h); (ii) KOH, EtOH, reflux (1 h).

of potassium hydroxide (6.23 mmol) in absolute ethanol (40 ml). The mixture was refluxed for 2 h and filtered. The filtrate was treated with 800 mg (14.3 mmol) of potassium hydroxide and refluxed for 1 h. Insolubles were eliminated by filtration and the solvent was evaporated. Water was added to the resultant solid and the mixture was filtered. A white solid separated after addition of an excess of tetramethylammonium chloride solution. The white solid was filtered, washed with water and ethyl ether, and dried in vacuum. Yield: 575 mg (73%) of (**1**). FTIR (KBr): $\nu(\text{cm}^{-1}) = 2972, 2901, \nu(\text{C-H}), 2523, \nu(\text{B-H}), 1482, 948, \nu[\text{N}(\text{CH}_3)_4]$. ^1H -FTNMR (400 MHz, CD_3COCD_3 , 25°C , TMS): δ 6.72 [s, 1^x , S-CH(OCH₂CH₃)-S], 6.18 [s, 1^y , S-CH(OCH₂CH₃)-S], 3.83 (q, 2^x , -CH₂-), 3.45 [s, 12, N(CH₃)₄], 3.35 (q, 2^y , -CH₂-), 1.20 (t, 3^x , -CH₃), 1.03 (t, 3^y , -CH₃), -2.5

(broad, 1, B-H-B). Calcd. for $\text{C}_9\text{H}_{28}\text{B}_9\text{NOS}_2$: C, 32.98; H, 8.61; N, 4.27. Found: C, 31.76; H, 8.60; N, 4.52. The NMR data can be accounted for by the coexistence of the *cis* and *trans* isomers (indicated with superscripts x and y in the data) with a relative ratio of 1:2; however, at present we are not able to assign the signals with certainty.

Preparation and characterization of 7,8-(1',3'-dithia-2'-triphenylphosphoniumpropane-1',3'-diyl)-7,8-dicarbanido-undecaborate(12) (2) (Scheme 2). Under a dinitrogen atmosphere, 290 mg (0.885 mmol) of (**1**) were added to deoxygenated absolute ethanol (60 ml) containing 320 mg (1.22 mmol) of triphenylphosphine and 5 drops of 12 M HCl. The mixture was refluxed for 4 h. During that time a white solid appeared. The hot mixture was filtered, and

Scheme 2. Synthesis of **2**.

the solid was washed with boiling ethanol and ethyl ether and dried under vacuum. Yield: 284 mg (68%). FTIR (KBr): $\nu(\text{cm}^{-1}) = 3058, \nu(\text{C}_{\text{aryl}}-\text{H}), 2890, \nu(\text{C}-\text{H}), 2550, 2538, 2525, \nu(\text{B}-\text{H}), 1482, 1438, 1105, 750, 724, 686, \nu(\text{PPh}_3)$. ^1H -FTNMR (400 MHz, CDCl_3 , 25°C , TMS): δ -2.2 (broad, 1, B-H-B), 6.73 (s, 1, S-CHPPH₃-S), 7.98–7.80 [m, 15, P(C₆H₅)₃]. ^{11}B -FTNMR (128 MHz, CH_3COCH_3 , 25°C , $\text{BF}_3 \cdot \text{Et}_2\text{O}$): δ -7.9 (1B), -10.2 [d, $^1J(\text{B},\text{H}) = 121$ Hz, 2B], -18.8 [d, $^1J(\text{B}-\text{H}) = 133$ Hz, 4B], -30.1 (1B), -32.5 [d, $^1J(\text{B},\text{H}) = 176$ Hz, 1B]. Anal. Calcd. for $\text{C}_{21}\text{H}_{26}\text{B}_9\text{PS}_2$: C, 53.57, H, 5.56. Found: C, 53.52, H, 5.65.

X-Ray crystallography. Crystal data, details of data collection and structure refinement are summarized in Table 1. The lattice parameters are very close to those of

Table 1. Crystal data, data collection and structure refinement.

$\text{C}_{21}\text{H}_{26}\text{B}_9\text{PS}_2$	$\Theta = 10\text{--}14^\circ$
$M_r = 470.84$	$V = 2449$ (2) \AA^3
Monoclinic	$Z = 4$
$P2_1/n$	$D_x = 1.277$ Mg m^{-3}
$a = 11.373$ (3) \AA	Mo K_α
$b = 14.654$ (3) \AA	$\lambda = 0.71069$ \AA
$c = 14.694$ (6) \AA	$\mu = 0.288$ mm^{-1}
$\beta = 89.48$ (3) $^\circ$	$T = 295$ K
Lattice parameters from 25 reflections	Colourless needles, $0.40 \times 0.35 \times 0.28$ mm
Nicolet P3F four-circle diffractometer	ω scan, scan speed $1.5\text{--}15^\circ \text{min}^{-1}$
Absorption correction: none	$T_{\text{min}} = 0.987, T_{\text{max}} = 1.000$
6123 measured reflections	$R_{\text{int}} = 0.023$
5609 independent reflections	$\Theta_{\text{max}} = 27.5^\circ$
3021 observed reflections, criterion $ F > 3\sigma(F)$	3 standard reflections, frequency 60 reflections, variation 2%
$h_{\text{min}} = 0$	$h_{\text{max}} = 14$
$k_{\text{min}} = 0$	$k_{\text{max}} = 18$
$l_{\text{min}} = -19$	$l_{\text{max}} = 19$
Part of H-atoms refined	Refinement on F
$R = 0.087$	339 parameters
$R_w = 0.064$	3021 reflections in refinements
$S = 2.87$	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\text{max}} = 0.29$	$\Delta\rho_{\text{min}} = -0.3$ $e \text{\AA}^{-3}$
Extinction correction: none	$\Delta\rho_{\text{max}} = 0.4$ $e \text{\AA}^{-3}$
	Atomic scattering factors included in the XTAL2.6 system ¹⁰

a tetragonal unit cell, but the real symmetry is monoclinic. The structure was solved by direct methods by using the *SHELXS86* program.⁹ Least-squares refinements and all subsequent calculations were performed using the *XTAL* program system,¹⁰ which minimized the function $\sum w(\Delta F)^2$ [$1/w = \sigma^2(F_0)$]. After refinement of all non-hydrogen atoms with anisotropic thermal parameters, a subsequent difference Fourier map revealed all hydrogen atoms of the carbaborane cage. The hydrogen atoms of the cage, except for one H atom of B(10), were refined in the final cycles. The rest of the hydrogen atoms were placed at their calculated positions ($\text{C}-\text{H} = 1.00$ \AA and $U = 0.06$ \AA^2) and not refined. Refinement of this atomic arrangement, with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms, reduced the R -value to 0.087 ($R_w = 0.064$). The somewhat high R -value is a consequence of poor statistics of weak reflections.

Results and discussion

Fractional atomic coordinates and U_{eq} values for the non-hydrogen atoms are given in Table 1, and a drawing of the molecule is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. The five-membered sulfur heterocycle fused to the carbon atoms of the dicarbaborane cage is substituted at C(1) with the phosphorus atom of the triphenylphosphonium unit. Thus the positive charge of the phosphorus atom neutralizes the negative charge of the dicarbaborate. The phosphorus atom has replaced the *equatorial* hydrogen of the methylene group of the string. The S(1), C(7), C(8), S(2), C(1) ring adopts the *envelope* conformation, with the carbon atom C(1) *anti* with respect to the pentagonal C_2B_3 open face. The reduction of molecular symmetry from C_s to C_1 may be the result of packing conditions.

In the *nido*-carbaborane cage each boron atom is bonded to one hydrogen atom, except for B(10), which is bonded to two. The 'extra' proton is oriented towards the missing boron atom position of the fourth level. A cage with a short external S,S'-connected string is clearly rigid, and no great differences in the bond parameters would be expected when it coordinates as ligand to a metal. However, comparison of compound (**2**) with two metal complexes adopting different coordination modes, $[\text{RuCl}\{7,8\text{-}\mu\text{-(SCH}_2\text{S)}\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}(\text{PPh}_3)_2]$ ⁶ and

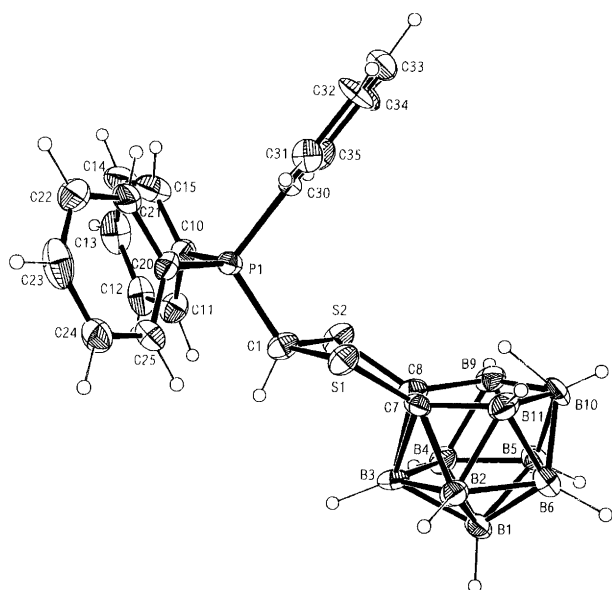


Fig. 1. ORTEP drawing of 7,8-(1',3'-dithia-2'-triphenylphosphoniumpropane-1',3'-diyl)-7,8-dicarba-nido-undecaborate(12). Thermal ellipsoids are drawn at 30% probability scale.

Table 2. Non-hydrogen coordinates and equivalent isotropic thermal parameters (in Å²) for 7,8-μ-[SCH(PPH₃)S]-7,8-C₂B₉H₁₀.

Atom	x/a	y/b	z/c	U _{eq} ^a
P(1)	0.1198(1)	0.1938(1)	0.2730(1)	0.038(1)
S(1)	-0.0304(1)	0.0576(1)	0.3689(1)	0.048(1)
S(2)	0.0005(2)	0.0497(1)	0.1675(1)	0.055(1)
C(1)	-0.0118(5)	0.1255(4)	0.2655(4)	0.047(4)
C(7)	-0.1005(5)	-0.0377(4)	0.3184(4)	0.038(4)
C(8)	-0.0830(5)	-0.0432(4)	0.2141(4)	0.043(4)
C(10)	0.1412(5)	0.2523(4)	0.1678(4)	0.043(4)
C(11)	0.0483(5)	0.2636(4)	0.1052(4)	0.055(5)
C(12)	0.0688(6)	0.3095(5)	0.0245(4)	0.069(5)
C(13)	0.1803(7)	0.3462(5)	0.0073(4)	0.081(6)
C(14)	0.2676(5)	0.3382(5)	0.0681(5)	0.070(5)
C(15)	0.2472(5)	0.2930(5)	0.1477(4)	0.067(5)
C(20)	0.1109(5)	0.2707(4)	0.3675(4)	0.041(4)
C(21)	0.2120(5)	0.3195(4)	0.3918(4)	0.058(5)
C(22)	0.2104(5)	0.3790(5)	0.4623(5)	0.066(5)
C(23)	0.1070(7)	0.3930(5)	0.5099(4)	0.074(5)
C(24)	0.0033(5)	0.3487(4)	0.4854(4)	0.056(5)
C(25)	0.0042(5)	0.2884(4)	0.4148(4)	0.048(4)
C(30)	0.2452(5)	0.1206(4)	0.2910(4)	0.038(4)
C(31)	0.2828(5)	0.1041(4)	0.3792(4)	0.051(4)
C(32)	0.3788(5)	0.0477(5)	0.3921(4)	0.058(5)
C(33)	0.4342(6)	0.0110(4)	0.3193(5)	0.063(5)
C(34)	0.3971(5)	0.0238(4)	0.2318(4)	0.060(5)
C(35)	0.3024(5)	0.0796(4)	0.2164(4)	0.056(5)
B(1)	-0.2981(6)	-0.1225(5)	0.2489(5)	0.047(5)
B(2)	-0.2349(6)	-0.0793(5)	0.3517(5)	0.045(5)
B(3)	-0.2252(6)	-0.0152(5)	0.2503(5)	0.045(5)
B(4)	-0.2007(6)	-0.0887(5)	0.1594(5)	0.048(5)
B(5)	-0.1943(6)	-0.2019(5)	0.2017(5)	0.054(5)
B(6)	-0.2171(6)	-0.1964(5)	0.3244(5)	0.056(5)
B(9)	-0.0628(6)	-0.1466(5)	0.1778(5)	0.054(5)
B(10)	-0.0770(6)	-0.2169(5)	0.2779(6)	0.063(6)
B(11)	-0.0977(6)	-0.1353(5)	0.3696(5)	0.051(5)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

[Hg{7,8-μ-(SCH₂S)-7,8-C₂B₉H₁₀}(PPh₃)],¹¹ reveals different orientation of the C(1) atom and some significant variations in bond parameters. In the Ru(II) complex the carbaborane moiety acts as tridentate ligand coordinating through the sulfur atoms and the hydrogen atom bonded to B(3), and orientation of the CH₂ group is *syn* with respect to the C₂B₃ open face. According to our earlier findings, *syn* orientation for the *S,S'*-connected strings is preferred when the coordination is *S,S'*.^{1-4,6} In [Hg{7,8-μ-(SCH₂S)-7,8-C₂B₉H₁₀}(PPh₃)] the metal has replaced the 'extra' proton at B(10) and adopts n³ coordination to the open face of the cage, and orientation of the CH₂ group is *anti* with respect to the C₂B₃ open face. Dihedral angles between the planes through C(7),S(1),S(2),C(8) and S(1),C(1),S(2) are 149.3(4)° in compound (2), -119.4(3)° in the Ru(II) compound and 137.6(4)° in the Hg(II) compound. The differences indicate considerable flexibility in the C(carbaborane)-S-C(1) group. Moreover, orientation of the bridging C(1) atom between the two sulfur atoms varies with the coordination mode of the metal atom in the complexes. In the Hg compound the *anti* orientation of the CH₂ group evidently is due to the repulsion between the metal and the CH₂ group. The bond lengths and angles in the three cages are approximately equal, but some significant differences are observed in the S(1),C(7),C(8),S(2),C(1) string. The S-C(1) distances [1.799(7)-1.827(6) Å] and S-C(carbaborane) distances [1.778(6)-1.801(4) Å] do not vary much, but the C(7)-C(8) distances and S(1)-C(1)-S(2) angles of the derivatives are significantly different. In compound 2, and in the Hg compound with C(1) *anti* with respect to the C₂B₃ open face, the C(7)-C(8) distances [1.547(8) and 1.566(6) Å] and S(1)-C(1)-S(2) angles [109.4(3) and 108.1(3)°] are not significantly different. As a consequence of the tridentate coordination of the carbaborane ligand in the Ru complex, with Ru *anti* and C(1) *syn* with respect to the C₂B₃ open face, the

Table 3. Selected bond lengths (in Å) and angles (in °).

S(1)-C(1)	1.827(6)	P(1)-C(1)	1.805(6)
S(1)-C(7)	1.774(6)	P(1)-C(10)	1.782(6)
S(2)-C(1)	1.822(6)	P(1)-C(20)	1.791(6)
S(2)-C(8)	1.791(6)	P(1)-C(30)	1.806(6)
C(7)-C(8)	1.547(8)	C(7)-B(3)	1.775(9)
C(8)-B(3)	1.748(9)	C(7)-B(11)	1.62(1)
C(8)-B(9)	1.62(1)	B(9)-B(10)	1.80(1)
B(10)-B(11)	1.82(1)		
C(1)-P(1)-C(10)	108.7(3)	C(1)-S(1)-C(7)	97.5(3)
C(1)-P(1)-C(20)	110.8(3)	C(1)-S(2)-C(8)	97.2(3)
C(1)-P(1)-C(30)	109.6(3)	S(1)-C(1)-S(2)	109.4(3)
C(10)-P(1)-C(20)	112.1(3)	S(1)-C(1)-P(1)	109.9(3)
C(10)-P(1)-C(30)	108.1(3)	S(2)-C(1)-P(1)	109.1(3)
C(20)-P(1)-C(30)	107.4(3)	S(1)-C(7)-C(8)	113.6(4)
S(1)-C(7)-B(3)	117.0(4)	S(2)-C(8)-C(7)	113.7(4)
S(2)-C(8)-B(3)	115.1(4)	C(7)-C(8)-B(9)	113.0(5)
C(8)-B(9)-B(10)	104.8(5)	B(9)-B(10)-B(11)	103.8(5)
B(10)-B(11)-B(7)	103.9(5)	B(3)-C(7)-C(8)	63.1(4)
B(3)-C(8)-C(7)	64.9(4)	C(7)-B(3)-C(8)	52.1(3)

C(7)–C(8) distance increases to 1.603(5) Å. Surprisingly, too, the S(1)–C(1)–S(2) angle decreases to 99.9(2)°, possibly indicating angle strain at C(1) in the Ru complex.

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